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(54) Title: DECOLORIZING COMPOSITIONS (57) Abstract <p>The present invention is directed to an indicator system for use in a detergent composition, the indicator system comprising a dye particle and a bleach particle, wherein the bleach particle has at least on first binder coating, wherein the dye particle initially colors the solvent and upon dissolution of the binder coating, the solvent subsequently substantially decolorizes by oxidation.</p>		

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DECOLORIZING COMPOSITIONS

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FIELD

10 The present invention relates to decolorizing compositions for use in detergent compositions comprising a bleach and a dye, whereby substantial decolorization takes place by oxidation.

BACKGROUND

15 Dyes are common ingredients in detergent compositions. There are many reasons that dyes are added to detergent compositions. One reason is for product appearance. Dyes are added to detergent compositions to make colored detergent compositions. A colored detergent composition can be entirely the same color or can have more than one color. For example, granular
20 detergent compositions which are in the form of white granules may contain colored "speckles" such as blue or green granular materials, which are mixed in the composition among the white granules. Consumers sometimes associate better cleaning ability with detergent compositions having such colored "speckles". For example, some consumers may associate white detergent
25 compositions containing colored "speckles" as special performing cleaning "actives" and believe these "actives" make the detergent composition clean better.

 In addition to product appearance, dyes are added to detergent compositions so that when the detergent compositions are placed in a solvent,
30 e.g. a wash liquor, the dye colors the solvent and the appearance of the color is noticeable to consumers. Because the change in color of the solvent is noticeable to the human eye, the dyes can be used as a visual indicator. For example, a denture cleansing composition may comprise a dye which colors the denture soaking solution. The appearance change of the color of the denture
35 soaking solution from a color, such as blue, to a clear color indicates to the

consumer that the dentures have been sufficiently soaked in the solution and thus is clean.

5 In order to have a desirable indicator, the dye needs to change the color appearance of the solvent to a noticeable color after the detergent composition is first added to the solvent. Then, the decolorization should occur over a predetermined amount of time. The decolorization of the dye must be timed in accordance to the length of time of the indicated event. Thus, it is desired to control the rate of decolorization in order to have an effective indicator.

10 None of the existing art provides all of the advantages and benefits of the present invention.

SUMMARY

15 The present invention is directed to an indicator system for use in a detergent composition, the indicator system comprising a dye particle and a bleach particle, wherein the bleach particle has at least one first binder coating, wherein the dye particle initially colors a solvent and upon dissolution of the binder coating, the solvent subsequently substantially decolorizes by oxidation.

20 These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION

25 While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

All percentages are by weight of total composition unless specifically stated otherwise.

All ratios are weight ratios unless specifically stated otherwise.

30 As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

The indicator system of the present invention can be used in detergent compositions. The term "detergent composition" as used herein is intended to designate any of the agents conventionally used for removing soil, such as general household detergents or laundry detergents of the synthetic or soap type. The term is also intended to include other cleaning agents.

The present invention is directed to an indicator system for use in a detergent composition, the indicator system comprising a dye particle and a bleach particle, wherein the bleach particle has at least one first binder coating, wherein the dye particle initially colors a solvent and upon dissolution of the binder coating, the solvent subsequently substantially decolorizes by oxidation. The binder coating on the bleach delays the initiation of the oxidation process, thus controlling the length of time it takes to substantially decolorize the dye particle.

Although some dyes inherently have a long decolorization rate upon oxidation (e.g. over 36 hours), some dyes have a very short decolorization rate upon oxidation (e.g. immediately or within a few seconds). Depending upon the purpose of the indicator, it is beneficial to be able to prolong the time it takes for the dye to substantially decolorize upon oxidation. For example in one embodiment, if it is desired to indicate an event after a lapse of twenty seconds, the change in color of the solvent from color to substantially clear should be completed in twenty seconds. Thus for this embodiment, the number of first binder coatings on the bleach particle is related to the time it takes for the dye to substantially decolorize in twenty seconds.

The type of dye that can be used in the indicator system may be constrained by factors such as regulatory and safety restrictions, high cost of the material, etc. In addition, the type of dye that can be used may be limited due to the type of detergent composition in which the indicator system will be used. In that case, the type of dye that is available to be used is limited in number. In addition, different dyes have different decolorization rates upon oxidation due to the inherent characteristics of different dyes. It is thus beneficial to be able to choose a dye from such a limited list and control (e.g. lengthen) the time of decolorization of the dye so that the indicator system can be used appropriately as an indicator for a specific event.

Indicator System

Although not wanting to be limited by theory, the following narrative describes how the indicator system preferably operates. The indicator system comprises two separate particles, the dye particle and the bleach particle.

5 According to the present invention, the dye particle and the bleach particle are separate, free-flowing particles and are not meant to be a single agglomerate or otherwise physically made into one particle. The bleach particle is coated with at least one first binder coating. When detergent compositions comprising the indicator system is placed in a solvent, the dye particle first colors the solvent.

10 Next, upon dissolution of the binder coating (or binder coatings) of the bleach particle, oxidation takes place in the solvent and substantially decolorizes the dye. As a result, the solvent subsequently substantially decolorizes.

It is preferred that the initial coloring of the solvent is of a color that is noticeable to the human eye. In addition, the decolorization over time should be

15 sufficient for a person to notice the change in color. If the solvent substantially decolorizes instantaneously or very rapidly (e.g. within a few seconds or less), it will be difficult for the consumer to visually notice the change in color by looking at the solvent. Therefore, it is preferred that the indicator system makes the solvent change in color which is visually noticeable, as well as substantially

20 decolorize over time, in a time interval of about 5 seconds or more, preferably from about 10 seconds or more, until the color substantially disappears.

The preferred solvent is water. Other solvents besides water can also be used. Organic solvents are preferred. A suitable organic solvent for this invention is an organic solvent which has a flash point of 10°C and above. Non

25 limiting examples of solvents include alcohols such as ethanol, propanol, glycerol, polyethylene glycol, propanediol, dipropylene glycol n-butyl ether, or any compound such as benzene sulfonic acid or its salt, toluene sulfonic acid or its salt, or xylene sulfonic acid or its salt. Mixtures of solvents can also be used.

If the solvent is water, the decolorization that takes place is preferably in a

30 water having a pH of from about 2 to about 13, preferably from about 7 about 12. Separately, a preferred indicator system is placed in a solvent having a temperature from about 5°C to about 50°C, more preferably from about 20°C to about 40°C.

The indicator system can be used in many ways. For example, a denture

35 cleaning composition can contain an indicator system of the present invention in

order to notify the consumer when the denture has been sufficiently soaked in the solvent for cleaning. The indicator system can also be used in sterilizing compositions in order to notify the user that the items are sufficiently sterilized when soaked for the appropriate predetermined amount of time. Depending
5 upon the purpose of the indicator system, it is desirable to control the rate of decolorization.

In one preferred embodiment of the invention, the indicator system can be used in a detergent composition which signals the minimum predissolving time of the detergent composition in a solvent. The indicator system initially colors the
10 solvent in a visually noticeable color. Preferably, users may associate the appearance of color to mean that the detergent composition is "activated" or otherwise have improved cleaning ability. Upon a lapse of time, the solvent substantially decolorizes. Preferably, users will associate the decolorization to mean that the detergent composition has been sufficiently dissolved in the
15 solvent. In actuality, the detergent composition may only be partially, and not completely, dissolved. In this embodiment, it is preferred that the lapse of time for decolorization be in the range of from about 5 seconds to about 60 seconds, preferably from about 10 seconds to about 30 seconds.

A. Bleach Particle

20 The bleach particle is one component of the indicator system.

For granular detergent compositions, the average particle size of the bleach particle with the coating (or coatings) is important. If the size is too small, the bleach particles will fall to the bottom of the detergent composition and segregate from the remaining detergent composition components. This is
25 undesirable since when the consumer uses the detergent, the dosage amount of the composition extracted from upper portion of the detergent package may not contain the bleach particle, since most of the bleach particles may have segregated to the bottom of the package. Therefore, preferably for granular detergent compositions, the size of the bleach particle including the coating (or
30 coatings) and particulate layer (or layers), if included, is from about 2000 microns to 100 microns, preferably from about 200 to 800 microns.

1. Bleach

The bleach particle is made of a bleach. Preformed peracid bleach, peroxygen bleach, and any bleach activator which liberates peracid are
35 preferred. Non limiting preferred peroxygen bleaches include perborate and

percarbonate bleaches. Chlorine bleaches can also be used. The bleach should preferably have a melting point of higher than about 70°C, preferably higher than about 100 °C, to avoid melting, or otherwise decomposing when the first binder coating is used to coat the bleach in order to form the bleach particle.

- 5 Preferably, the average particle size of the bleach is smaller than about 800 microns, more preferably less than about 400 microns.

Oxygen bleaches useful in the present invention can be any of the oxidizing agents known for laundry, hard surface cleaning, automatic dishwashing or denture cleaning purposes. Oxygen bleaches or mixtures thereof
10 are preferred, though other oxidant bleaches, such as oxygen, an enzymatic hydrogen peroxide producing system, or hypohalites such as chlorine bleaches like hypochlorite, may also be used.

Oxygen bleaches deliver "available oxygen" (AvO) or "active oxygen" which is typically measurable by standard methods such as iodide/thiosulfat
15 and/or ceric sulfate titration. See the well-known work by Swern, or Kirk Othmer's Encyclopedia of Chemical Technology under "Bleaching Agents". When the oxygen bleach is a peroxygen compound, it contains -O-O- linkages with one O in each such linkage being "active". AvO content of such an oxygen bleach compound, usually expressed as a percent, is equal to $100 \times \frac{\text{number of active oxygen atoms}}{\text{molecular weight of the oxygen bleach compound}}$.
20

The oxygen bleach herein can have any physical form compatible with the intended application; more particularly, liquid-form and solid-form oxygen bleaches as well as adjuncts, promoters or activators are included. Liquids can
25 be included in solid detergents, for example by adsorption onto an inert support; and solids can be included in liquid detergents, for example by use of compatible suspending agents.

Common oxygen bleaches of the peroxygen type include hydrogen peroxide, inorganic peroxohydrates, organic peroxohydrates and the organic
30 peroxyacids, including hydrophilic and hydrophobic mono- or di- peroxyacids. These can be peroxycarboxylic acids, peroxyimidic acids, amidoperoxycarboxylic acids, or their salts including the calcium, magnesium, or mixed-cation salts. Peracids of various kinds can be used both in free form and as precursors known as "bleach activators" or "bleach promoters" which, when combined with a source
35 of hydrogen peroxide, perhydrolyze to release the corresponding peracid.

Also useful herein as oxygen bleaches are the inorganic peroxides such as Na_2O_2 , superoxides such as KO_2 , organic hydroperoxides such as cumene hydroperoxide and t-butyl hydroperoxide, and the inorganic peroxyacids and their salts such as the peroxosulfuric acid salts, especially the potassium salts of peroxodisulfuric acid and, more preferably, of peroxomonosulfuric acid including the commercial triple-salt form sold as OXONE by DuPont and also any equivalent commercially available forms such as CUROX from Akzo or CAROAT from Degussa. Certain organic peroxides, such as dibenzoyl peroxide, may be useful, especially as additives rather than as primary oxygen bleach.

Mixed oxygen bleach systems are generally useful, as are mixtures of any oxygen bleaches with the known bleach activators, organic or inorganic catalysts, enzymatic catalysts and mixtures thereof; moreover such mixtures may further include brighteners, photobleaches and dye transfer inhibitors of types well-known in the art.

Preferred oxygen bleaches, as noted, include the peroxohydrates, sometimes known as peroxyhydrates or peroxohydrates. These are organic or, more commonly, inorganic salts capable of releasing hydrogen peroxide readily. They include types in which hydrogen peroxide is present as a true crystal hydrate, and types in which hydrogen peroxide is incorporated covalently and is released chemically, for example by hydrolysis. Typically, peroxohydrates deliver hydrogen peroxide readily enough that it can be extracted in measurable amounts into the ether phase of an ether/water mixture. Peroxohydrates are characterized in that they fail to give the Riesenfeld reaction, in contrast to certain other oxygen bleach types described hereinafter. Peroxohydrates are the most common examples of "hydrogen peroxide source" materials and include the perborates, percarbonates, perphosphates, and persilicates. Other materials which serve to produce or release hydrogen peroxide are, of course, useful. Mixtures of two or more peroxohydrates can be used, for example when it is desired to exploit differential solubility. Suitable peroxohydrates include sodium carbonate peroxyhydrate and equivalent commercial "percarbonate" bleaches, and any of the so-called sodium perborate hydrates, the "tetrahydrate" and "monohydrate" being preferred; though sodium pyrophosphate peroxyhydrate can be used. Many such peroxohydrates are available in processed forms with coatings, such as of silicate and/or borate and/or waxy materials and/or surfactants, or have particle geometries, such as compact spheres, which

improve storage stability. By way of organic peroxohydrates, urea peroxyhydrate can also be useful herein.

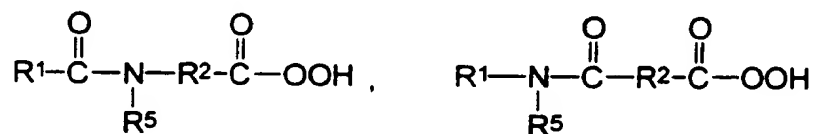
Percarbonates and perborates are widely available in commerce, for example from FMC, Solvay, Mitsubishi Gas Chemical, Nippon Peroxide and Tokai Denka.

Organic percarboxylic acids useful herein as the oxygen bleach include magnesium monoperoxyphthalate hexahydrate, available from Interlox, *m*-chloro perbenzoic acid and its salts, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid and their salts. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred oxygen bleaches also include 6-nonylamino-6-oxoperoxyacaproic acid (NAPAA) as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al, and include those having formula HO-O-C(O)-R-Y wherein R is an alkylene or substituted alkylene group containing from 1 to about 22 carbon atoms or a phenylene or substituted phenylene group, and Y is hydrogen, halogen, alkyl, aryl or -C(O)-OH or -C(O)-O-OH.

Organic percarboxylic acids usable herein include those containing one, two or more peroxy groups, and can be aliphatic or aromatic. When the organic percarboxylic acid is aliphatic, the unsubstituted acid suitably has the linear formula: HO-O-C(O)-(CH₂)_n-Y where Y can be, for example, H, CH₃, CH₂Cl, COOH, or C(O)OOH; and n is an integer from 1 to 20. Branched analogs are also acceptable. When the organic percarboxylic acid is aromatic, the unsubstituted acid suitably has formula: HO-O-C(O)-C₆H₄-Y wherein Y is hydrogen, alkyl, alkyhalogen, halogen, or -COOH or -C(O)OOH.

Monoperoxydicarboxylic acids useful as oxygen bleach herein are further illustrated by alkyl percarboxylic acids and aryl percarboxylic acids such as peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g., peroxy- α -naphthoic acid; aliphatic, substituted aliphatic and arylalkyl monoperoxy acids such as peroxyauric acid, peroxysearic acid, and N,N-phthaloylaminoperoxyacaproic acid (PAP); and 6-octylamino-6-oxoperoxyhexanoic acid. Monoperoxydicarboxylic acids can be hydrophilic, such as peracetic acid, or can be relatively hydrophobic. The hydrophobic types include

those containing a chain of six or more carbon atoms, preferred hydrophobic types having a linear aliphatic C8-C14 chain optionally substituted by one or more ether oxygen atoms and/or one or more aromatic moieties positioned such that the peracid is an aliphatic peracid. More generally, such optional substitution by ether oxygen atoms and/or aromatic moieties can be applied to any of the peracids or bleach activators herein. Branched-chain peracid types and aromatic peracids having one or more C3-C16 linear or branched long-chain substituents can also be useful. The peracids can be used in the acid form or as any suitable salt with a bleach-stable cation. Very useful herein are the organic percarboxylic acids of formula:



or mixtures thereof wherein R^1 is alkyl, aryl, or alkaryl containing from about 1 to about 14 carbon atoms, R^2 is alkylene, arylene or alkarylene containing from about 1 to about 14 carbon atoms, and R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms. When these peracids have a sum of carbon atoms in R^1 and R^2 together of about 6 or higher, preferably from about 8 to about 14, they are particularly suitable as hydrophobic peracids for bleaching a variety of relatively hydrophobic or "lipophilic" stains, including so-called "dingy" types. Calcium, magnesium, or substituted ammonium salts may also be useful.

Other useful peracids and bleach activators herein are in the family of imidoperacids and imido bleach activators. These include phthaloylimidoperoxycaproic acid and related arylimido-substituted and acyloxynitrogen derivatives. For listings of such compounds, preparations and their incorporation into laundry compositions including both granules and liquids, See U.S. 5,487,818; U.S. 5,470,988, U.S. 5,466,825; U.S. 5,419,846; U.S. 5,415,796; U.S. 5,391,324; U.S. 5,328,634; U.S. 5,310,934; U.S. 5,279,757; U.S. 5,246,620; U.S. 5,245,075; U.S. 5,294,362; U.S. 5,423,998; U.S. 5,208,340; U.S. 5,132,431 and U.S. 5,087,385.

Useful diperoxyacids include, for example, 1,12-diperoxydodecanedioic acid (DPDA); 1,9-diperoxyazelaic acid; diperoxybrassicic acid; diperoxysebacic acid and diperoxyisophthalic acid; 2-decyldiperoxybutane-1,4-dioic acid; and 4,4'-sulphonylbis(diperoxybenzoic acid). Owing to structures in which two relatively hydrophilic groups are disposed at the ends of the molecule, diperoxyacids have

sometimes been classified separately from the hydrophilic and hydrophobic monoperacids, for example as "hydrotropic". Some of the diperacids are hydrophobic in a quite literal sense, especially when they have a long-chain moiety separating the peroxyacid moieties.

5 More generally, the terms "hydrophilic" and "hydrophobic" used herein in connection with any of the oxygen bleaches, especially the peracids, and in connection with bleach activators, are in the first instance based on whether a given oxygen bleach effectively performs bleaching of fugitive dyes in solution thereby preventing fabric graying and discoloration and/or removes more
10 hydrophilic stains such as tea, wine and grape juice - in this case it is termed "hydrophilic". When the oxygen bleach or bleach activator has a significant stain removal, whiteness-improving or cleaning effect on dingy, greasy, carotenoid, or other hydrophobic soils, it is termed "hydrophobic". The terms are applicable also when referring to peracids or bleach activators used in combination with a
15 hydrogen peroxide source. The current commercial benchmarks for hydrophilic performance of oxygen bleach systems are: TAED or peracetic acid, for benchmarking hydrophilic bleaching. NOBS or NAPAA are the corresponding benchmarks for hydrophobic bleaching. The terms "hydrophilic", "hydrophobic" and "hydrotropic" with reference to oxygen bleaches including peracids and here
20 extended to bleach activator have also been used somewhat more narrowly in the literature. See especially Kirk Othmer's Encyclopedia of Chemical Technology, Vol. 4., pages 284-285. This reference provides a chromatographic retention time and critical micelle concentration-based set of criteria, and is useful to identify and/or characterize preferred sub-classes of hydrophobic,
25 hydrophilic and hydrotropic oxygen bleaches and bleach activators that can be used in the present invention.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the
30 sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

On a different track from the bleach activators illustrated herein above,
35 another suitable hydrogen peroxide generating system is a combination of a C₁ -

C4 alkanol oxidase and a C1 -C4 alkanol, especially a combination of methanol oxidase (MOX) and ethanol. Such combinations are disclosed in WO 94/03003. Other enzymatic materials related to bleaching, such as peroxidases, haloperoxidases, oxidases, superoxide dismutases, catalases and their enhancers or, more commonly, inhibitors, may be used as optional ingredients in the instant compositions.

2. First Binder Coating

The bleach particle is coated with at least one first binder coating. In addition, the bleach particle can be coated with more than one first binder coating. The number of coatings can depend on what time interval is desired for the decolorization to take place. The more coatings the bleach particle has, the longer it takes for the decolorization to take place. Preferably, the bleach particle has at least three coatings or more. If more than one coating is used, it is preferred to have a particulate layer between each pair of binder coatings. Preferably, it is beneficial to let the binder coating set before applying multiple binder coatings.

A non limiting list of preferred binder coatings include methyl cellulose, carboxymethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, sodium alginate, guaiac gum, gum arabic, gelatin, casein, collagen, chitin, chitosan, polyvinyl alcohol, sodium polyacrylate, polyethylene oxide, polyoxyethylene oxypropylene copolymers, polyvinyl pyrrolidone, and other such water-soluble macromolecules; propyl naphthalenesulfonate, butyl naphthalenesulfonate, formaldehyde condensates of naphthalenesulfonates, other naphthalenesulfonate-based surfactants, linear alkylbenzenesulfonates with carbon number of 8 to 22, α -olefinsulfonates with carbon number of 8 to 22, polyoxyethylene alkyl ether sulfuric acid esters with carbon numbers of 8 to 22, alkylphosphoric acid esters with carbon numbers of 8 to 22, and other such anionic surfactants; and polyoxyethylene alkyl ethers with carbon numbers of 8 to 22, polyoxyethylene alkyl phenyl ethers with carbon numbers of 8 to 22, sorbitan fatty acid esters with carbon numbers of 8 to 22, glycerol fatty acid esters, and other such nonionic surfactants. Such water-soluble macromolecules or surfactants may be used individually or jointly, and they may also be used singly or as combinations of two or more components. Water may also be used as a binder coating.

The first binder coating has the following preferred physical characteristics. It preferably has a melting point of about 40°C to 70°C. The coating has preferably a viscosity at the time of coating so that the binder form is easily sprayed onto the bleach in order to form the bleach particle. The preferred
5 viscosity is from about 10 centipoise (cP) to about 100 cP for first binder coatings which have a melting point of about 40°C to 70°C.

If there is more than one binder coating, each binder coating thickness may vary. Each binder preferably has an average thickness of about 10 microns to about 15 microns.

10 3. Particulate Layer

Although not wanting to be limited by theory, having a particulate layer between each pair of first binder coatings allows the bleach particle to be spherically coated in several layers of first binder coatings. As stated previously, it is sometimes desirable to have multiple layers in order to delay the time
15 substantial decolorization takes place. In addition, it is preferred to have a particulate layer at the outermost layer of the bleach particle in order to have a free-flowing particle. In such an embodiment, the bleach particle is coated with a particulate layer as the outermost layer.

Preferred material to be used as a particulate layer include zeolite, sodium
20 silicate (dry form), layered sodium silicate, silica, sulfate, carbonate, and mixtures thereof. The material for the particulate layer has an average particle size smaller than about 50 microns, preferably smaller than about 10 microns, more preferably from about 1 micron to about 10 microns.

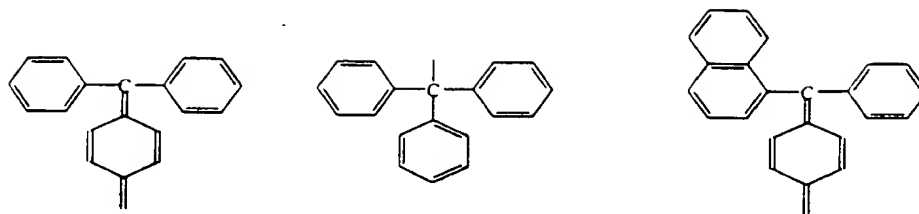
B. Dye Particle

25 The dye particle is another component of the indicator system. The dye particle preferably has an average particle size of from about 1 micron to about 250 microns, preferably from about 1 micron to about 100 microns.

1. Dye

30 The dye particle includes a dye. The dye becomes substantially colorless and/or substantially decolorizes when oxidized. Any commercially available dyes may be used. Preferably, the dyes do not stain the cleaning surface.

Preferably, such dyes are selected from a triphenylmethane- or diphenylmethane-based dye having the following partial structure:



Specific examples of such dyes include C.I. Acid Green 5, C.I. Acid Green 9, C.I. Acid Green 74, C.I. Acid Violet 49, and C.I. Acid Blue 7. The C.I. numbers and nomenclature relate to references in the "Colour Index - Second Edition 1956" published by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists.

C. I. Basic Green 4, C. I. Basic Violet 3, C. I. Acid Green 3, and C. I. Acid Green 5, F. D. & C. Violet Number 1 are particularly preferred dyes.

Preferred dyes are which substantially decolorizes over a predetermined time. As used throughout, the term "decolorization" includes both complete decolorization as well as substantial decolorization. Substantial decolorization means that decolorization should be in an amount of at least 50%, and preferably 75%. The numerical determination of these values is effected colorimetrically by measuring the extinction within the region of the maximum light absorption. Since in colorimetric measurements, clouds of the solution, such as are frequently present in solvents, e.g. wash solutions, are disturbing, clouds must be removed by filtration, centrifuging or other methods. If this is not possible, the test should be effected with model substances, i.e., with mixtures of substances which contain all detergent composition components, with the exception of those which interfere with the colorimetric measurement.

In one embodiment of the present invention, the dye particle is made of only a dye and the dye particle does not have a core, a second binder coating, or powder material.

2. Core

The dye particle preferably includes a core, although it is not required. The core can be made of one or a mixture of components. Preferably, the core is made of a composition of alkaline inorganic or organic salts commonly incorporated in detergent compositions such as alkali metal carbonates, silicates, phosphates, and polyphosphates, or alkaline salts of amino polycarboxylic acids, and mixtures thereof. Also preferable are neutral inorganic salts, such as alkali

metal sulphates and chlorides, soaps and/or organic synthetic detergents, enzyme pills, and mixtures thereof. The core may also contain any other conventional detergent ingredients and/or additives, and mixtures thereof.

5 The core preferably has a melting point of above 70°C, more preferably of above 100°C.

3. Second Binder Coating

10 If the core is used as part of the dye particle, the core is preferably coated with at least one second binder coating. The second binder coating is the same type of coating material as the first binder coating discussed above. There is no requirement that the first binder coating and the second binder coating must be exactly the same material. For example, the bleach particle's first binder coating can be methyl cellulose and the dye particle's second binder coating can be a nonionic surfactant, in one embodiment of the present invention. In addition, the second binder coating has the same physical properties as the first binder coating.

15 If the dye particle contains a core and a second binder coating, the dye is added to the outer surface of the second binder coating. When there is more than one second binder coating, it is to be noted that the dye is added to the outer surface of the last layer of the second binder coating and not between any two second binder coatings.

20 In one preferred embodiment of the present invention, the dye particle has a particulate layer (as described above) as an outermost layer for free flowing purposes of the dye particle.

25 In another preferred embodiment of the present invention, the dye and a powder material are first pre-mixed before applying the mixture to the coat d core to form a dye particle, thereby forming a free flowing dye particle. In this method, it is not necessary to have an additional particulate layer as the outermost layer in order to have a free flowing dye particle.

30 The powder material is any fine, powder material. The preferred average particle size of the premixture of dye and the powder material is from about 1 to about 10 microns. The type of powder material is the same as the particulate layer material described above, and also has the same physical properties.

35 The indicator system is made by the following method: providing a dye particle; providing a bleach; coating the bleach with at least one first binder coating to form a bleach particle; and combining the dye particle and the bleach

particle to form an indicator system, wherein the dye particle and bleach particle remain separate particles. The term "combining" with respect to the dye particle and the bleach particle to form an indicator system does not mean physically combine or agglomerate the two particles.

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Examples

The following examples further describe and demonstrate the preferred embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration, and are not to be construed as limitations of the present invention since many variations thereof are possible without departing from its spirit and scope.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from the scope of the present invention.

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Example 1

This example shows how to make an embodiment of the indicator system of the present invention. A premixture is made of C. I. Acid Green 5 dye, and the following powder materials: zeolite, silica and methyl cellulose. A core, comprising surfactant, carbonate, silicate, and polymers are placed in a mixer and agitated in the mixer. A second binder coating of nonionic surfactant in a liquid form at 40°C is sprayed into the mixer. The cores are coated with the second binder coating to form a one-layered coated core. Next, the premixture of dye and powder materials are added into the mixer to cover the outer layer of the coated cores. The total mixing time is about three minutes.

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Next, the bleach particle is made by taking sodium percarbonate into a mixer and agitating the bleach. A first binder coating of nonionic surfactant in a liquid form at 40°C is sprayed into the mixer to form a coated bleach. Then a particulate layer of zeolite is added to the mixer to cover the outer surface of the coated bleach. After the first layer of coating for the bleach, a second layer is similarly applied. A second layer of first binder coating is sprayed into the mixer. Then another particulate layer of zeolite is added to the mixer to cover the outer surface of the twice-coated bleach. A third layer of first binder coating is added

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in the same way as the other two layers. Finally, the outer surface of the coated bleach is covered with zeolite.

Of the dye particle, about 1% is made of the dye, about 9% is made of the powder materials, and about 60% is made of the core material. Of the bleach particle, 59% is made of sodium percarbonate bleach, 3.5% is made of the first layer of the first binder coating, 7.5% is made of the first layer of the particulate layer, 4.1% is made of the second layer of the first binder coating, 10.3% is made of the second layer of the particulate layer, 1.9% is made of the third layer of the first binder coating, 14.6% of the particulate layer as the outermost surface layer. The decolorization rate of this embodiment is about 15 to 20 seconds upon oxidation in water having a temperature of about 20°C - 30°C having a pH of 11.

Example 2

This example shows how to make another embodiment of the indicator system of the present invention. The dye particle only consists of a dye (C. I. Basic Violet 3). The bleach particle is made by taking sodium perborate into a mixer and agitating the bleach. A first binder coating of polyvinyl alcohol in a liquid form at 40°C is sprayed into the mixer to form a coated bleach. No other binder coatings are added. The outer surface of the coated bleach is covered with zeolite as a particulate layer.

Of the dye particle, about 100% is made of the dye. Of the bleach particle, 70% is made of sodium perborate bleach, 10% is made of the first layer of the first binder coating, 20% is made of the particulate layer. The decolorization rate of this embodiment is about 5 seconds upon oxidation in a solvent having a temperature of about 20°C - 30°C having a pH of 11.

WHAT IS CLAIMED IS:

1. An indicator system for use in a detergent composition, the indicator system comprising:
 - a. a dye particle; and
 - b. a bleach particle, wherein the bleach particle has at least one first binder coating,wherein the dye particle initially colors a solvent and upon dissolution of the first binder coating, the solvent subsequently substantially decolorizes by oxidation.
2. The indicator system of Claim 1, wherein the bleach particle has at least two first binder coatings and wherein the bleach particle further comprises a particulate layer between each pair of first binder coatings.
3. The indicator system of Claim 1, wherein the bleach particle further comprises a particulate layer as an outermost layer of the bleach particle.
4. The indicator system of Claim 1, wherein the dye particle comprises:
 - a. a dye;
 - b. a core; and
 - c. at least one second binder coating.
5. A detergent composition comprising the indicator system of Claim 1.
6. An indicator system for use in a detergent composition which signals the minimum predissolving time of the detergent composition in a solvent, the indicator system comprising:
 - a. a dye particle; and
 - b. a bleach particle, wherein the bleach particle has at least three first binder coatings and wherein the bleach particle further comprises a particulate layer between the first and second layer of the first binder coatings and a second particulate layer between the second and third layer of the first binder coatings,

- 10 wherein the dye particle initially colors the solvent and upon dissolution of the binder coatings, the solvent subsequently substantially decolorizes by oxidation.
7. The indicator system of Claim 6, wherein the dye particle comprises a dye, a core, and at least one second binder coating, and wherein the bleach particle is further coated with the particulate layer as an outermost layer.
8. A method of making a dye particle and a bleach particle which form an indicator system for use in a detergent composition, the method comprising the following steps:
- 5 a. providing a dye particle,
b. providing a bleach,
c. coating the bleach with at least one first binder coating to form a bleach particle,
d. combining the dye particle and the bleach particle to form an indicator system, wherein the dye particle and bleach particle
10 remain separate particles.
9. The method of Claim 8, wherein the bleach particle has at least two first binder coatings and wherein the bleach particle further comprises a particulate layer between each pair of first binder coatings.
10. A method of making a dye particle and a bleach particle which form an indicator system for use in a detergent composition, comprising the following steps:
- 5 a. providing a dye particle, wherein the dye particle is formed by:
(1) providing a core;
(2) coating the core with at least one second binder coating to form a coated core; and
(3) applying dye to the coated core to form a dye particle;
b. providing a bleach;
10 c. coating the bleach with at least three first binder coatings to form a bleach particle, wherein the bleach particle further comprises a particulate layer between the first and second layer of the first

- binder-coatings and a second particulate layer between the second and third layer of the first binder coatings; and
- 15 d. combining the dye particle and the bleach particle to form an indicator system, wherein the dye particle and bleach particle remain separate particles.
11. The method of Claim 10, wherein the bleach particle is coated with a particulate layer as an outermost layer.
12. The method of Claim 11, wherein the dye is pre-mixed with a powder material before applying the mixture to the coated core to form a dye particle.
13. The indicator system made by the process as in any one of Claims 8-12.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/13727

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C1103/40 C1103/39 C1103/395

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C110

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 195 42 830 A (HENKEL KGAA) 22 May 1997 see page 3, line 7 - line 36; claims; table 2	1,5,8,13
A	GB 1 281 796 A (UNILEVER) 12 July 1972 see page 2, line 38 - line 75; claims; examples	1,5,8,13
A	DATABASE WPI Section Ch, Week 8923 Derwent Publications Ltd., London, GB; Class A97, AN 89-170590 XP002060882 & JP 01 113 499 A (DAINICHISEIKA COLOR & CHEM MFG) , 2 May 1989 see abstract	1,5

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

Special categories of cited documents

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"S" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Inter- national Application No

PCT/US 97/13727

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	<p>PATENT ABSTRACTS OF JAPAN vol. 017, no. 516 (C-1112), 17 September 1993 & JP 05 140590 A (MANABISU:KK:OTHERS: 01), 8 June 1993, see abstract</p> <p style="text-align: center;">-----</p>	1.5

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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